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A major focus of our research has been on the development of techniques that permit direct visualization of surfactant microstructures. With complex microstructures like vesicles, liposomes or microtubules, where polydispersities and interactions are important issues, the abilities to directly observe real time behavior and structural details is important in characterizing amphiphilic systems. We have employed two techniques, video enhanced microscopy (VEM) and cryo-transmission electron microscopy (cryo-TEM).

We have been interested in characterizing surfactant aggregates in water as a function of temperature. The original stimulus for this work was the desire to understand how the unique structural properties of water affected self-assembly processes. Specifically the goal was to determine whether nonpolar groups are driven out of aqueous solution by the release of structured water (entropic effects), and that water is therefore different from all other sol-
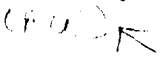
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19. continued.

vents. We studied micellization across a sufficiently large temperature range (25 to 160°C) so that water changed from a highly structured liquid to just another polar hydrogen bonded solvent.

We have shown that changing surfactant counterions can have a dramatic effect on aggregate structure. The key observation was that double-chained cationic surfactants like didodecyldimethylammonium form clear nonviscous solutions with acetate or hydroxide counterions up to quite high concentrations (C = 0.2 M). The corresponding bromides are opaque, liquid crystalline dispersions.

Much of our research program has focused on the structural properties of three-component microemulsions which employ the dialkyldimethylammonium halides as surfactants. We began by characterizing microemulsions formed from didodecyldimethylammonium bromide and the oils hexane through tetradecane. The key features of these systems are: (1) the surfactant is only sparingly soluble in either oil or water, so that the interfacial area is fixed by the surfactant concentration. (2) In the absence of co-surfactant, oil specificity becomes evident. (3) The single-phase region of the DDAB-cyclohexane microemulsion resembles a wedge with two well defined sides. These correspond to minimum (AB) and maximum water content curves which almost coincide with constant w/s lines on the ternary phase diagram. The significance of the curved upper boundary of the wedge can be understood in terms of the packing constraints. With decreasing oil penetration, the single-phase region shows progressively larger departure from this simple wedge shape, and with tetradecane the single phase does not extend into the oil corner. To a first approximation however, it is convenient to picture the phase diagram as comprising a wedge. (4) Upon addition of water (as one moves from the AB line toward the water corner along constant s/o lines), the conductance decreases for all the oils except tetradecane, and a transition to a nonconducting liquid is observed. The locus of the percolation points defines another constant w/s line which lies just above the maximum water line. NMR self-diffusion measurements give D_{oil} and D_{DDAB} which are almost constant throughout the entire single-phase region. Those for oil are about 1/2 of that for bulk oil. Upon addition of water, D_{H_2O} decreases by a factor of 20, which substantiates the conductance measurements. Thus all of the DDAB microemulsions are bicontinuous along the AB line and, upon addition of water, all (except those containing tetradecane) transform to w/o microemulsions.

CHARACTERIZATION OF VESICLE AND MICROEMULSION MICROSTRUCTURES

FINAL REPORT

D. FENNELL EVANS

SEPTEMBER 1988

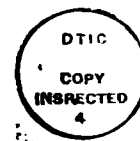U.S. ARMY RESEARCH OFFICE

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STATEMENT OF THE PROBLEM STUDIED

A. TO DEVELOP VIDEO ENHANCED CONTRAST DIFFERENTIAL INTERFERENCE MICROSCOPY (VECDIM) as an effective technique for characterizing surfactant microstructures (vesicles, liposomes, liquid crystals and emulsions). This new light microscope technique permits particles and microstructures with sizes down to 500Å to be directly visualized on a television screen. The growth, dynamics, transformation and fusion of such microstructures can be directly pictured, recorded on video tape and analyzed in real time. VECDIM constitutes a major advance for the characterization of colloidal phenomena since it is rapid, direct and free from artifacts.

A major thrust of the research involves developing VECDIM into an effective tool for characterizing microstructural systems. The emphasis will be on developing sample cells which will permit controlled flow and diffusion expeirments on vesicles, microemulsions and other determgent microstructures to be carried out. VECDIM will also be used to study solubilization of organic material in micellar and other surfactant microstructure solutions. The systems chosen are based on information obtained by the principal investigator in previous studies using the spinning disc technique. VECDIM permits the dissolution process to be directly pictured at the detergent-oil interface.

B. TO EXPLOIT THE ABILITY TO DICTATE THE ARCHITECTURE OF SURFACTANT MICROSTRUCTURES by controlling curvature and regulating particle-particle interactions. Many key problems in industrial and biological processes involve microstructures formed from surfactant aggregates, biopolymers and other colloidal materials. Industrial examples include detergency, decontamination of surfaces, enhanced oil recovery, filtration, membrane reactors, coating flow technology, mineral flotation, corrosion inhibition and porous media processes. In the biological domain transport of vesicles along microtubules, structure and reactivity of membranes including antibody binding are obvious examples. An emerging new technology involves the use of biological analogues of vesicles, liquid crystals and related microstructures in industrial processes like high resolution, fast photographic film (in which grain size is defined by vesicles), selective drug delivery, control of nucleation and growth of metal clusters, and controlled photosynthetic reactions.

The microstructural systems employed in industrial and biological processes are complex, usually polydisperse and sometimes (intentionally) inherently unstable. They can be extremely sensitive to changes in pH, ionic strenght, temperature, flow conditions, and surfactant concentration. The research described in this proposal addresses the question of how one controls surfactant structures. Specific projects include the following:

1. Vesicles and related surfactant aggregates: to develop a more complete characterization of the spontaneous vesicles that we have discovered. The study will address questions concerning micelle-vesicle equilbrium, flow stability and vesicle growth and transformation accompanying changes in chemical environment. Micelle-microtubule transformations will be searched for.

2. Three-component microemulsions: to elucidate the structure of three-component microemulsions using x-ray, light scattering, NMR and vapor phase measurements, examine low surface tension and to exploit various ways of controlling curvature.

C. TO DETERMINE THE AGGREGATION NUMBERS OF ALKYLTRIMETHYLAMMONIUM BROMIDES IN WATER OVER THE TEMPERATURE RANGES 25 TO 160°C. The driving force for surfactant aggregation

in water is the transfer of hydrocarbon chains from the polar aqueous environment to the oil-like interior of the aggregate. The forces responsible for such aggregation are also important in determining the staiblity of proteins, enzymes, macro- and microemulsions and play a major role in directing biological self-assembly. In order to understand such hydrophobic processes in more detail, we have determined critical micelle concentration (CMC) for alkyltrimethylammonium surfactants in water up to 160°C where the structural properties of water are greatly diminished. In addition we have characterized micelle and liquid crystal formation in two other polar solvents ethylammonium nitrate and hydrazine. Our conclusion concerning hydrophobic processes (described in detail below) are contrary to those commonly accepted.

In order to rigorously interpret the CMC data as a function of temperature, micelle aggregation numbers are required. The recent analytic solution to the spherical Poisson-Boltzmann equation provides the necessary theoretical framework. We will determine surfactant aggregation numbers for the alkyltrimethylammonium bromides in water as a function of temperature up to 160°C using classical light scattering.

SUMMARY OF RESULTS

(1) Direct Visualization of Surfactant Microstructures

A major focus of our research has been on the development of techniques that permit direct visualization of surfactant microstructures. With complex microstructures like vesicles, liposomes or microtubules, where polydispersities and interactions are important issues, the abilities to directly observe real time behavior and structural details is important in characterizing amphiphilic systems. We have employed two techniques [1], video enhanced microscopy (VEM) and cryo-transmission electron microscopy (cryo-TEM).

A video enhanced microscope consists of a light microscope equipped with differential interference contrast optics, a video camera and a computer for image processing. In light microscopy, contrast limitations restrict the size of aggregates we can select for study, while resolution limitations restrict the amount of structural information we can extract from microscopic observation. Many surfactant aggregates like vesicles and microtubules are of inherently low contrast, and the eye cannot distinguish them from the background solution even with differential interference contrast optics. We can overcome this limitation by using a video camera that responds linearly to intensity and a computer capable of real-time digital image processing.

Two important image-processing steps are (1) background subtraction and (2) grey-scale transformation. Background subtraction removes optical noise arising from inaccessible dirt and lens imperfections. This noise appears as a mottled background pattern that obscures the objects of interest. We can remove it by storing the mottled image in the computer and subtracting it frame by frame from the actual pattern. Grey-scale transformation increases the contrast between image and background. With very low contrast images (such as small unilamellar vesicles) all the information may be contained in only 20 of the 256 grey levels detected by the video camera. The transformation process changes all the levels above and below these 20 grey levels to black and white respectively and expands the original 20 shades of grey into 256 shades.

As a result of this contrast enhancement, we can detect isolated colloidal particles like unilamellar vesicles or latex spheres as small as 60 nm or extended structures as

small as 10 to 60 nm [2], and this enables us to visualize the bilayer structure of large vesicles and liposomes. However, the video image is enlarged because of diffractions.

The main advantages of VEM are that it gives us the ability to (1) observe the dynamics of amphiphilic structure in real-time without perturbing the system, (2) follow flow and/or chemically-induced transformations, (3) record the video information and reanalyze the data at a later time, and (4) use time-lapse recording to follow transformations that occur over a period of hours or days. It is useful to remember that photographs of the video images convey only a small fraction of the information we can obtain in a video film.

Neutralization of didodecyldimethylammonium hydroxide micelles by hydrogen bromide involves all these factors. The change of counterion results in the transformation of a clear micellar solution (aggregation number 40) [3] to liposomes and bilayers. Simple mixing of the two solutions between the coverslip and slide results in uncontrolled convection and an almost explosive formation of large liposomes [1]. However, we can obtain more useful information about such transformations using a microscopic flow cell. In our cell (Fig. 1), the two solutions are pumped into two entrance ports so that a sharp interface forms down the length of the rectangular channel. When the flow is stopped, neutralization takes place across the interface. The micelle-liposome transformation (Fig. 2) occurs via "worms" or microtubules that are oriented preferentially in the direction of the acid-base concentration gradient. These "worms" disappear as liposomes form. We note that many transformations between various microstructures appear to involve "worms" as intermediates.
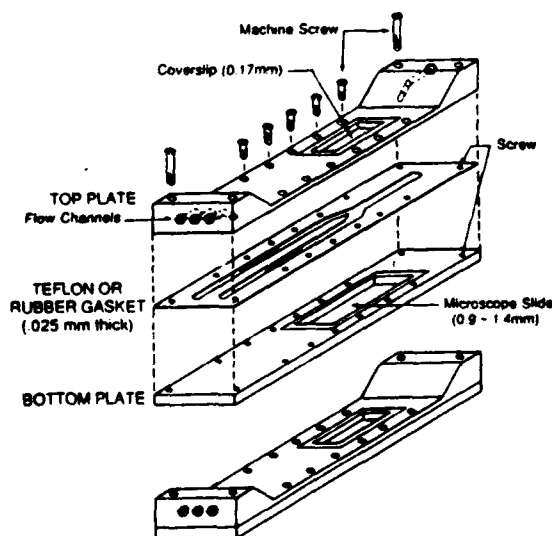

Figure 1. Microscope flow cell used to determine the effect of flow and to examine chemically induced transformations with VEM. In the configuration shown, the center of the three ports would be closed while solution and reagent would enter the outer ports, flow down the channels cut in the gasket, and join at the channel intersection, forming a sharp interface.
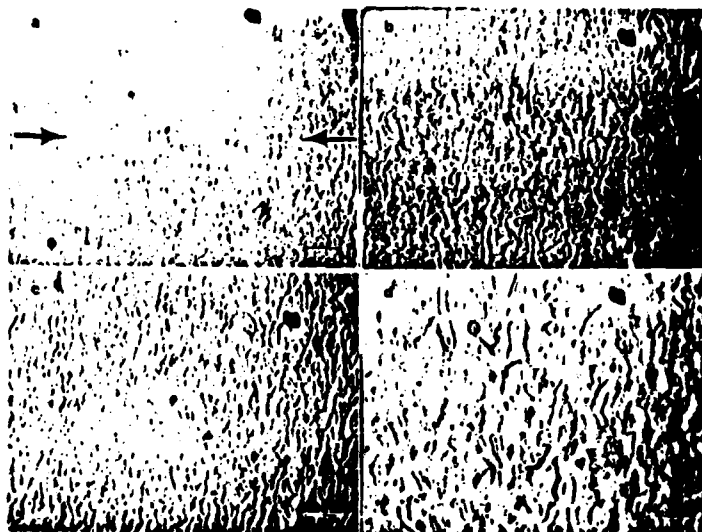

Fig. 2. Sequence of structures formed upon neutralization of 10^-3 M didodecyldimethylammonium hydroxide by HBr in the flow cell and examined with VEM (Fig. 3). Bar = 10 μm.
(a) Zero time — 2C₁₂R2C₁OH–HBr interface formed by initial left to right flow is indicated by arrows. Clear field is acid solution at top. Growing vesicles are in the lower portion of the micrograph.
(b) One minute after the flow stops — particles grow and "worms" begin to form.
(c) Ten minutes later — solution filled with "worms" with preferential orientation in the direction of the acid-base concentration gradient.
(d) Forty-five minutes later — "worms" have transformed into spherical particles which slowly grow.

We have developed a number of cells for special VEM applications. In order to use high magnification (100X objective, oil immersion), the total working space between the condenser and objective lens is limited to 2 mm and standard microscopes and coverslips must be employed. In our stainless steel flow cell, this criterion is met by gluing a microscope slide to the bottom plate of the cell and a coverslip to the top plate, and setting the distance between the glass surfaces by insertion of a thin teflon gasket. The cell can be used in two modes: as a flow cell (shown above with a Y-shaped flow channel) or as a stop flow mixing cell in which two solutions are mixed in a T-tube mixer attached to the cell. The mixed solution is flowed into the cell down a single channel, stopped, and the transformation followed and recorded on video tape.

We have also developed a thermostatted cell which employs a microscope slide coated on the back with a transparent conducting layer of tin oxide [4]. The sample is placed on the slide, covered with a coverslip and heated by passing a current through the oxide layer. The temperature is measured by a thermocouple. (Commercially available thermo-statted cells are too thick to use with the VEM optics, and do not provide a uniform heating of the sample.) In addition we have built a flow cell for measuring electro-phoretic mobility, which permits the structure of the particles whose mobility is being measured to be observed simultaneously. Using this cell, we have made measurements on small vesicles prepared from mixtures of single- and double-chained surfactants, meas-urements which could not have been carried out with commercially available equipment. Finally, we have developed flow cells which permit the dissolution of water-insoluble material by surfactants to be followed visually. These applications are illustrated in the discussions below.

Fig. 3. VEM micrograph of 1.7% SHBS. Bar = 10 μm.
A,B — Liposomes (birefringent under crossed polars).
C — Large vesicle containing entrapped smaller vesicles.
D — Vesicle with a "dust-storm" appearance in real time, indicating that it is filled with small, unresolvable particles.

Figure 3 (a sample of a six-month-old, 1.7 wt% SHBS) shows a typical polydisperse liquid crystal-line aggregate with a wide diver-sity of structures. When we switch the VEM optics to polarizing optics without moving the microscope slide, birefringence and the Maltese crosses characteristic of liquid crystalline liposomes appear in the large structures (points A and B, Fig. 3). We can follow the undula-tions of individual bilayers within the birefringent liposomes (point B, Fig. 3) and the caged movement of smaller vesicles entrapped within larger vesicles (point C, Fig. 3) in real time. Among the smaller structures that lie beyond the resolution limit of the light microscope, the "unstruc-tured" spherical region of diameter ~ 9 μM (point D, Fig. 3), is of particular interest. In real-time this region presents a "sand storm" appearance associated with very small structures.

In order to obtain more detailed structural information, we examined this SHBS sample by cryo-TEM [5]. In this technique, a thin liquid sample film is applied onto a carbon-film-covered TEM grid with many perforations. The grid is held by tweezers and inserted in a guillotine-type plunger. When the grid is plunged into liquid ethane, the

water in the specimen solidifies without crystallizing to form a vitreous ice matrix. Such rapid freezing avoids the artifacts produced by the phase separation and solute segregation encountered in many other TEM preparation techniques [6]. Formation of vit- rified specimens has several distinct advantages. Contrast improves because scattering from hexagonal ice is absent. As a consequence, the background becomes almost trans- parent, and we can see the fine infrastructure of vesicles, and individual bilayers. In addition, electron beam radiation damage is reduced in vitreous ice.
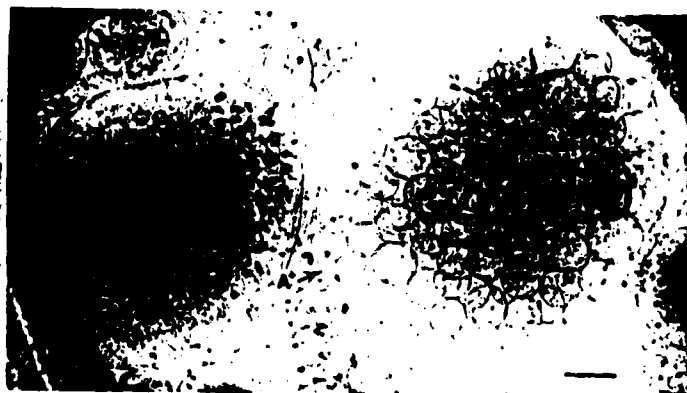

Fig. 4. Vitrified hydrated vesicles (VHV) cryo-TEM picture of a 1.7 wt% SHBS sample prepared with CWS. Note large (1.75 μm) single-walled vesicle (A) encapsulating many smaller vesicles. Bar = 0.15 μm.

Fig. 5. Electron micrograph of 1.7% SHBS showing vesicle-encapsulated microtubules. (A) Microtubule in the process of budding off to form small vesicles (B) coiled microtubule. Bar = 0.15 μm.

Figures 4 and 5 show several cryo- TEM pictures of the 1.7% SHBS. They reveal a variety of structures, includ- ing vesicles within vesicles, coiled tubules within vesicles, and liposomes in which the bilayer walls are visible in the clear field produced by the vitrified ice. Notice in Fig. 5 the appearance of beaded tubes which appear to have been frozen in the process of transforming to small unilamellar ves- icles (point A). The large birefrin- gent liposomal structures evidenced by polarizing microscopy and VEM probably are located in regions of vitrified ice that are too thick for viewing.

As a comparison of cryo-TEM and VEM results, the enclosed vesicle structure (point A, Fig. 5) of diameter 1.75 μm, which contains a large number of small unilamellar vesicles holds particular interest. We believe this structure is simi- lar to the VEM structure at point D in Fig. 3. In fact, the sequence of structures at point C, (Fig. 3, D = 15 μm), point D (Fig. 3, D = 9 μm), point A (Fig. 4, D = 1.75 μm) and point C (Fig. 5, D = 0.01 μm) suggest that cryo-TEM and VEM see a continuity of structures that differ in size, but are topologi- cally similar.

More recently we have obtained the first Cryo-TEM pictures of small spherical micelles (D ≈ 40Å) formed from ditetradecyldimethylammonium bromide.

(2) Effect of Temperature on Surfactant Microstructures

We have been interested in characterizing surfactant aggregates in water as a func- tion of temperature. The original stimulus for this work was the desire to understand how the unique structural properties of water affected self-assembly processes. Specif-

ically the goal was to determine whether nonpolar groups are driven out of aqueous solution by the release of structured water (entropic effects), and that water is therefore different from all other solvents. We studied micellization across a sufficiently large temperature range (25 to 160°C) so that water changed from a highly structured liquid to just another polar hydrogen bonded solvent.

We measured the CMCs (conductance) [7] and more recently the micellar aggregation numbers (light scattering) [8] for tetradecyltrimethylammonium bromide (and other alkyltrimethylammonium halides) from 25 to 160°C. These results are summarized in Fig. 6; for $C_{14}H_{29}N(Me)_3Br$, the CMC in water increases by a factor of 8 while the aggregation number decreases from 70 to 10.

The free energy of micellization can be expressed in terms of the dressed micelle model [9] as

$$RT \ln X_{CMC} = \Delta g(HP) + \Delta g(HG) \quad , \tag{1}$$

where $RT \ln X_{CMC}$ is the total free energy of micellization, $\Delta g(HP)$ is the free energy of transferring the hydrocarbon chain out of water and into the oil-like interior of the micelle, and $\Delta g(HG)$ is the free energy associated with the headgroup interaction. We can calculate $\Delta g(HG)$ from the nonlinear Poisson-Boltzmann equation in terms of the Debye length $1/\kappa$, the micellar aggregation number and the average headgroup area.

The important result, as shown in Fig. 7, is that the "hydrophobic" driving force for self-assembly is almost independent of temperature [10]. In fact the free energy displays a minimum at 90°, similar to what is observed for the solubility of rare gases in water [11]. The change in ΔG from 90° to 25° corresponds to increased solubility and leads to the conclusion that the effect of water structure, per se, is to actually stabilize nonpolar groups — not drive them out of aqueous solution.
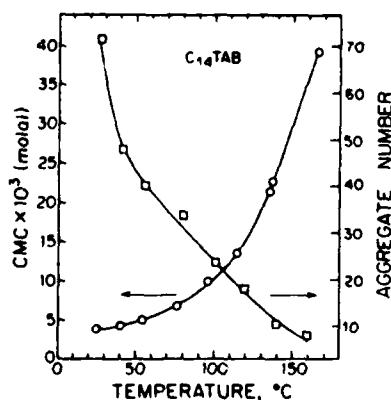

Figure 6. Micellization of tetradecyltrimethylammonium bromide (C_{14}TAB) in water as a function of temperature: the 10-fold increase in the critical micelle concentration (cmc) upon heating from 25 to 160 °C is shown (O); the decrease in micellar size (aggregation number) over the same temperature range is also shown (□).
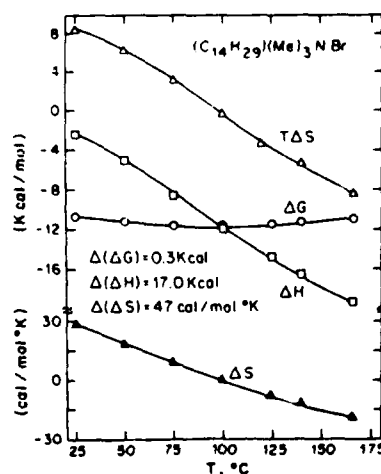
Figure 7. Thermodynamics of the micellization of tetradecyltrimethylammonium bromide obtained by using the dressed micelle model and the data in Figure 2. Despite large changes in ΔH and $T\Delta S$, the free energy of micellization (ΔG) remains almost constant across the entire temperature range from 25 to 160 °C.

Table 1 Comparison of Thermodynamics of Micelle Formation and Hydrocarbon Transfer in Water and Hydrazine

	surfactant	T, °C	$-\Delta G_{HP}$, kcal mol⁻¹	$-\Delta H_{HP}$, kcal mol⁻¹	ΔS_{HP}, cal mol⁻¹ K⁻¹
H_2O	$C_{14}TAB$	25	10.5	3.0	25
		95	11.5	12.4	-2.5
		16?	10.6	15.6	-12
H_4N_2	$C_{12}TAB$	35	7.1	11.0	-13
	$C_{12}OSO_3Na$	35	8.6	14.0	-18

Thermodynamics of Transfer of Nonpolar Gases from Cyclohexane to EtN_3NO_3 and H_2O

		$\Delta G°$, kcal mol⁻¹	$\Delta H°$, kcal mol⁻¹	$\Delta S°$, cal mol⁻¹ K⁻¹
Kr	FS*	1.6	-0.9	-9
	H_2O	2.8	-2.9	-19
CH_4	FS	1.6	-0.5	-4
	H_2O	2.9	-2.7	-18
C_2H_6	FS	2.0	-1.0	-10
	H_2O	3.9	-2.1	-20
C_4H_{10}*	FS	(3.61)	(-5.71)	(-31.3)
	H_2O	(6.35)	(-6.21)	(-42.1)

*The values for butane refer to the transfer from the gas phase to the fused salt and to water.
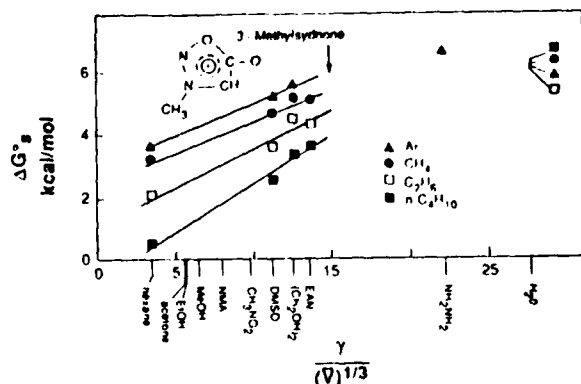

Figure 8. Free energy of transfer of argon, methane, ethane, and n-butane from several liquids to the gas phase. The liquids are plotted according to their value of $\gamma/v^{1/3}$ where γ is the surface tension and v is the molar volume. This (Gordon) parameter is a measure of a liquid's "cohesiveness", and liquids with Gordon parameters above about 13 tend to promote aggregation of amphiphilic molecules. One exception is the aprotic 3-methylsydnone where $\gamma/v^{1/3} \simeq 15$ but where no aggregation phenomena have been detected (see text).

The change in ΔG with temperature permits the value of ΔH and ΔS in Fig. 7 to be calculated. The very large changes in ΔH and ΔS compensate one another in such a way as to make almost no contribution to the free energy.

A complementary approach to this problem involves characterizing surfactant aggregation processes in other polar hydrogen bonding solvents like hydrazine [12] and ethylammonium nitrate [13]. In Table 1, the ΔG, ΔH and ΔS for water and hydrazine are compared. Water and hydrazine are equally solvophobic, and hydrazine at 25°C looks very much like water at 160°C.

A more general issue is what solvent properties are necessary to drive self-assembly of amphiphilic molecules. All of the solvents studies so far (H_4N_2, EAN, formamide, glycols) are polar, multiply hydrogen bonded solvents. A useful relationship between solvophobic free energy and solvent polarity is shown in Fig. 8, where ΔG is plotted against $\gamma/v^{1/3}$ [14,15]. This latter quantity is similar to the Hildebrand solubility parameter, but permits solvents with vanishingly small vapor pressure (EAN) to be considered. All of the non-hydrogen bonding solvents studied fall below the glycols, in which aggregation phenomena are greatly diminished. An exception is 3-methylsydnone which is a polar aprotic solvent ($\epsilon = 144$, $\mu = 7.4$, $\gamma/v^{1/3} = 15$) which falls between H_4N_2 and EAN in Fig. 8. All of our attempts [16] (conductance, polarized light microscopy, DIR) to obtain evidence for self-assembly of micelles or liquid crystals in this solvent were unsuccessful.

In summary, (1) comparison of micellar aggregation processes in water and other polar hydrogen solvents provides a way of identifying the unusual features of aqueous solutions. (2) Studies across a large temperature range in water provdes a way to assess the contributions of water structure to amphiphilic aggregation, and (3) measurements in 3-methylsydnone provides evidence that self-assembly processes require a solvent with multiple hydrogen bonding sites.

A second major issue involves the effect of temperature on aggregate structure. The size of all ionic aggregates appears to decrease with increasing temperature, as exemplified by the data in Fig. 6. One often cited explanation, that these decreases reflect

changes in water structure is ruled out by the data in Fig. 7. Since this data pertains to the CMC when interaggregate interactions are small, the decrease in aggregation number must reflect changes in headgroup interactions, i.e. must be of electrostatic origin. It occurred to us that the dielectric constant at the surface of the charged aggregates might have a temperature dependence which was significantly different from that of the bulk. The interfacial dielectric constant is lower than the bulk value because of image effects associated with the adjacent hydrocarbon core and partial orientation of the interfacial water, and could therefore have a very different temperature dependence. We measured the interfacial dielectric constant, ε', from 25 to 90°C using solvatochromic dye probes [17]. While there is good reason to be skeptical about the absolute magnitude of ε' determined by such techniques, the temperature dependence is probably more reliable. The value of $\varepsilon'kT$ shows a slight positive temperature dependence, whereas that for the bulk dielectric constant displays a slight negative dependence. However, the differences are not significant. We plan to pursue the question of headgroup interactions as a function of temperature as part of the proposed research.

Double-chained surfactants display considerably more diversity in their changes of aggregate structure with temperature. We will explore this subject as part of our proposed research program. As an initial effort [4,18], we have examined the aggregation behavior of the dialkyldimethylammonium bromides as a function of temperature with VEM, cryo-TEM and fluorescence probe-quencher measurements. With the VEM heating stage, we observe the transformation of $(C_{10}H_{21})_2N(Me)_2Br$ from liquid crystalline liposomes to single-wall vesicles which upon further heating disappear (T > 70°C) suggesting the formation of micelles which cannot be detected by VEM. Cryo-TEM measurements on didecyldimethylammonium bromide solutions heated to 70°C, before quenching in liquid ethane, show the presence of small USV and possibly the existence of small micellar structures [1]. Thus, upon heating, this surfactant transforms from liposome structures with a surfactant number of $v/\ell a \approx 1$ to spherical micelles with $v/\ell a > 1/3$.

More direct evidence for this can be obtained from fluorescence lifetime measurements. These studies constitute a substantive part of last year's research program and since they are not yet published they will be discussed in some detail. Our measurements employed pyrene or octylpyrene as the fluorescence probe with a probe-to-surfactant ratio less than 2×10^{-4} and dibutylaniline as quencher. Fluorescence lifetime measurements were made using a single photon counting technique.

For a micellar solution, the data were fitted to the miceller quenching model

$$I(t) = I(0) \exp\left[A_2 t - A_3(1 - \exp(- A_4 t))\right] \qquad (2)$$

where A2 and A4 are the rate constant for unquenched decay of fluorescence (k_1) and for quenching of a probe by a single quencher. A3 represents the average number of quenchers per micelle and is given by

$$A_3 = \frac{[Q] \cdot i}{[SURF] - [CMC]} = \bar{n} \qquad (3)$$

where [Q] is the quencher concentration, [SURF] is the surfactant concentration, [CMC] is the critical micelle concentration, i is the average aggregation number. For dilute monodisperse micelles in which probe and quencher exchange between micelles can be ignored, i is the weight average aggregation number n. Plots of $\ln(I/I_0)$ vs. time yield curves with a double exponential decay like those shown in Fig. 9A for hexadecyltrimethylammonium acetate which forms spherical micelles with $\bar{n} = 68$.

We have developed an analogous expression for fluorescence lifetimes in liposomes and vesicle dispersions which is

$$I(t) = I(0) \exp\left[-k_1 t - k_v[Q_a]t - k_D[Q_a]t^{1/2}\right] , \qquad (4)$$

where k_v is the second order rate constant for quenching in vesicles, etc., k_D is a "diffusion-depletion" term that accounts for time dependent reaction rates in viscous solvents (like amphiphilic bilayers) and Q_a is the quencher concentration calculated using the total aggregate volume (not the bulk solution volume). Equation (4) can be rewritten as

$$I(t) = I(0) \exp\left(-k_{app}t - k_{DO}t^{1/2}\right) , \qquad (5)$$

where $k_{app} = k_1 + k_v[Q_a]$ and $k_{DO} = K_D[Q_a]$. Plots of k_{app} and k_{DO} vs. $[Q_a]$ allow diffusion coefficients and reaction encounter distances between probe and quencher to be calculated. Thus solution containing 100% micelles (Fig. 9A, hexadecyltrimethylammonium acetate) or 100% vesicles (Fig. 9B, 1.9 mM sonicated egg lecithin, SUV) can be easily distinguished by the slopes of their respective decay curves. For mixtures of micelles and vesicles

$$I(t) = I(0)\left\{f_m \exp\left[-A_2 t - A_3(1 - \exp - A_4 t)\right]\right.$$

$$\left. + (1-f_m)\left[\exp\left(-k_{app}t - K_{DO}t^{1/2}\right)\right]\right\} , \qquad (6)$$

where f_m is the fraction of surfactant in micellar form. We tested this equation by generating simulated fluorescence data and were able to extract back the input using eq. (7). However, when we added Gaussian noise like that encountered in actual fluorescence data, we were unable to extract back the original parameters. Alternatively, if the data from micelle-vesicle mixtures is fit to eq. (2) (the micelle model), the values of A4 show a marked dependence on quencher concentration which increases as $(1-f_m)$ increases. Thus we can obtain a quantitative estimate of the relative fractions of micelles and vesicles; in particular, we can follow vesicle-to-micelle transition and can obtain an estimate of micellar aggregation numbers. Measurements on dialkyl-dimethylammonium bromide systems as a function of temperature yield curves which transform from those of Fig. 9B at low temperature to those of Fig. 9A
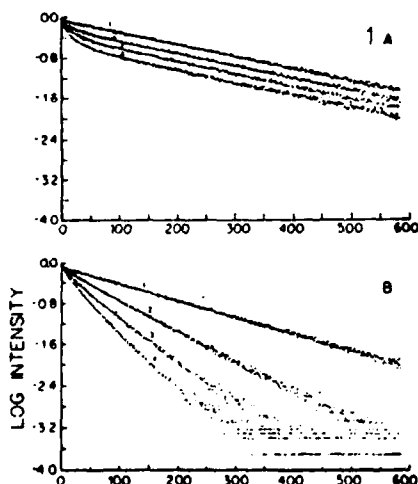
Fig. 9. Single photon counting data (normalized to the maximum intensity) for a) 0.03 M hexadecyltrimethylammonium acetate (CTAOAc), 1 – n = 0.0, 2 – n = 0.00541, 3 – n = 0.0106, 4 – n = 0.0162; b) 1.9 mM egg lecithin (small unilamellar vesicle, SUVs, in 0.115 M NaCl prepared by the alcohol injection method), 1 – n = 0.0, 2 – n = 0.017, 3 – n = 0.0214, 4 – n = 0.0320;

at high temperature. At intermediate temperatures the data fit eq. (6). These results are consistent with the VEM and cryo-TEM images.

We also investigated the behavior of mixtures of dicaproylphosphatidylcholine, which

forms small spherical micelles, and dipalmitoylphosphatidylcholine, which forms multi-layer liposomes [10]. In this case the isothermal transformation from micelles to liposomes is driven by changes in chain length. The fluorescence measurements yield data which demonstrate the coexistence of mixtures of vesicles and micelles in the mixed amphiphilic system.

(3) Effect of Counterions Upon Amphiphilic Structures

We have shown that changing surfactant counterions can have a dramatic effect on aggregate structure. The key observation was that double-chained cationic surfactants like didodecyldimethylammonium form clear nonviscous solutions with acetate or hydroxide counterions up to quite high concentrations (C = 0.2 M) [19]. The corresponding bromides are opaque, liquid crystalline dispersions.

Some insight into this behavior comes form a comparison of the micellar properties of single-chain compounds like dodecyltrimethylammonium bromide, hydroxides and acetates [20]. The acetates and hydroxides give high CMCs, considerably lower aggregation numbers and higher fractional micellar changes than the bromide. In addition, the micellar aggregation numbers increase only slightly with added NaOAc or NaOH (i.e. they change from 40 with no salt, to 68 at 1 M NaOH or NAOAc), whereas those for the bromide increase dramatically. Calculations with the dressed micelle model are consistent with OH^- and OAc^- counterions sitting on the average 4Å further away from the surface than do Br^- ions in the corresponding bromide [21]. In the case of OAc^- and OH^- counterions, the high degree of aggregate ionization leads to larger headgroup repulsion and an increase in curvature at the aggregate-water interface. At the other extreme are some of the chlorobenzoates which bind more strongly than bromide, and result in the formation of extended viscoelastic structures even with single-chained surfactants.

Recently, we have measured the aggregation number, N, for hexadecyltrimethylammonium bromide-acetate mixtures. A plot of N vs. mole fraction OAc^- is linear, going from 122 for the pure bromide to 75 for the acetate.

With a change in counterion from Br^- to OAc^- or OH^-, dialkyldimethylammonium surfactants form clear solutions containing either vesicles, micelles or a mixture. We originally proposed, based on inferences drawn from QELS, VEM and transmission electron microscopy, that didodecyldimethylammonium hydroxide and acetate formed vesicles in dilute solution which transform into micelles in more concentrated solution [19,22]. Steady state fluorescence-quencher measurements supported the hypothesis of a vesicle-to-micelle transformation. However, there are a number of implicit assumptions in using steady state fluorescence measurements for measurement of aggregation numbers. For that reason, we reinvestigated didodecyldimethylammonium acetate using the lifetime measurements described in the previous section. The results are consistent with the presence of mainly micelles across the entire composition range. These conclusions are in accord with neutron scattering measurements by Professor L. Magid [23].

We have also investigated microstructures formed from mixtures of ditetradecyldimethylammonium bromide and acetate using VEM, cryo-TEM, video enhanced electrophoresis and time resolved fluorescence quenching [4,24]. A gradual transformation from multilamellar liposomes, to unilamellar vesicles and microtubules, and then to small spherical micelles occurs as the bromide to acetate ratio goes from unity to zero. Fluorescence quenching reveals that micelles and larger aggreates (i.e. microtubules and vesicles) coexist at intermediate bromide to acetate ratios. Electron microscope pictures of

these acetate systems reveal the presence of single component spherical micelles, and constitute the first direct visualization of spherical micelles by VEM.

Replacement of counterions with anionic surfactants can also result in the formation of aggregates with increased curvature. For example, addition of the macrocyclic cryptate, C222, to sodium dodecylsulfate results in a decrease in aggregation number from 60 to 40 [25,26]. Addition of C222 to the double-chained Texas I results in the conversion of liposomes to vesicles (at low ratios of C222 to surfactant) and micelles at higher ratios [27]. The C222 has a diameter of 1 nm, and complexation of alkali metal ions re-

(4) Microemulsions

Much of our research program has focused on the structural properties of three-component microemulsions which employ the dialkyldimethylammonium halides as surfactants. We began by characterizing microemulsions formed from didodecyldimethylammonium bromide and the oils hexane through tetradecane [28-31]. The key features of these systems are: (1) the surfactant is only sparingly soluble in either oil or water, so that the interfacial area is fixed by the surfactant concentration. (2) In the absence of co-surfactant, oil specificity becomes evident. (3) The single-phase region of the DDAB-cyclohexane microemulsion resembles a wedge with two well defined sides (see Figs. 10 and 11). These correspond to minimum (AB) and maximum water content curves which almost coincide with constant w/s lines on the ternary phase diagram. The significance of the curved upper boundary of the wedge can be understood in terms of the packing constraints described below. With decreasing oil penetration, the single-phase region shows progressively larger departure from this simple wedge shape, and with tetradecane the single phase does not extend into the oil corner. To a first approximation however, it is convenient to picture the phase diagram as comprising a wedge. (4) Upon addition of water (as one moves from the AB line toward the water corner along constant s/o lines), the conductance decreases for all the oils except tetradecane, and a transition to a nonconducting liquid is observed. The locus of the percolation points defines another constant w/s line which lies just above the maximum water line
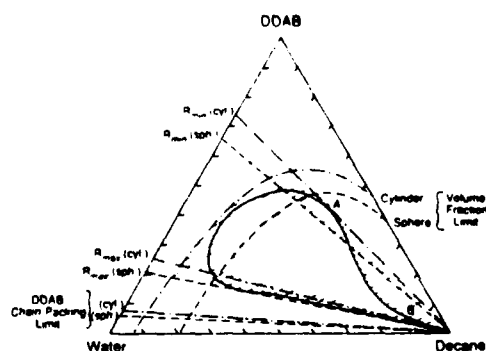

Figure 10. Boundaries allowed by geometric constraints due to volume fraction and surfactant chain packing with decane as the oil and $a_0 = 60$ Å^2 for DDAB. The actual phase boundary for DDAB-decane-water microemulsion systems is shown (solid line). R_{min} and R_{max} were derived from the onset at A point and percolation line (as the limiting radius of curvature for cylinders), respectively.
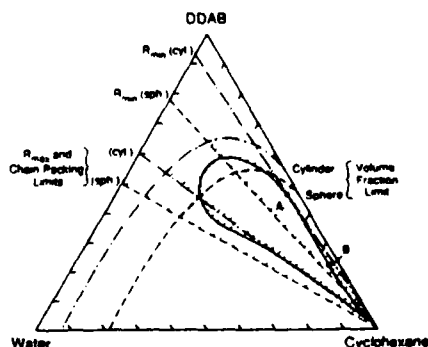

Figure 11. Boundaries allowed by geometric constraints due to volume fraction and surfactant chain packing with cyclohexane as the oil and $a_0 = 50$ Å^2 for DDAB. The actual phase boundary for cyclohexane-water-DDAB microemulsion systems is shown (solid line). R_{min} and R_{max} were derived from the onset at A point and percolation line (as the limiting radius of curvature for cylinders), respectively. These lines lie coincidentally on the same boundaries for surfactant chain packing limits at $a_0 = 50$ Å^2.

(located just above the R_{max} (cyl) lines in Figs. 10 and 11). NMR self-diffusion measurements give D_{oil} and D_{DDAB} which are almost constant throughout the entire single-phase region. Those for oil are about 1/2 of that for bulk oil. Upon addition of water, D_{H_2O} decreases by a factor of 20, which substantiates the conductance measurements. Thus all of the DDAB microemulsions are bicontinuous along the AB line and, upon addition of water, all (except those containing tetradecane) transform to w/o microemulsions.

Based on these observations, we have proposed that along the AB line the predominant structures are water-filled conduits which are interconnected to form a bicontinuous structure. Upon addition of water, or upon traversing the AB line, the conduits transform to droplets of water in oil. We have suggested that for any given oil there is a range of curvatures $R_{min} < R < R_{max}$ at the internal oil-water-surfactant interface that is compatible with the existence of the microemulsion phase. This curvature is determined by a balance between oil penetration into the surfactant layer, which tends to increase curvature, and headgroup repulsion, which tends to diminish curvature.
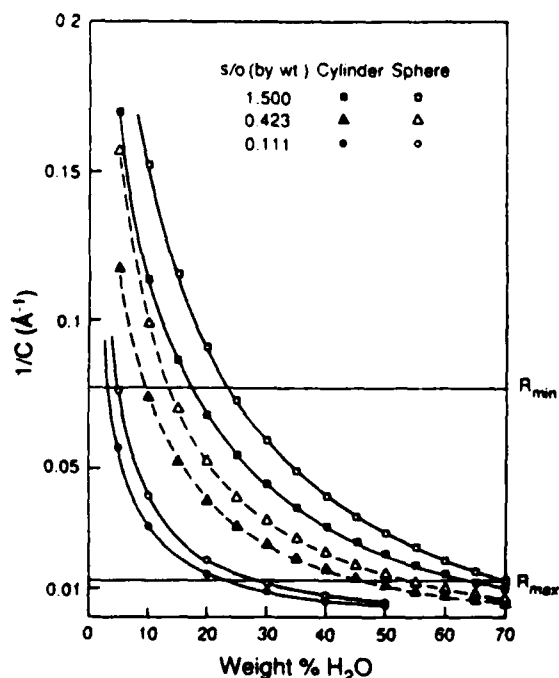

We have developed a geometric model [32] in terms of the packing constraints associated with surfactant-coated conduits and spheres of water. These constraints result in the phase diagram shown by the shaded region of Figs. 10 and 11 for two values of the headgroup area, 50 and 60Å^2. For comparison purposes, the microemulsion region of the decane and cyclohexane microemulsions are shown. This approach permits global microemulsion structure and curvature at the oil-water interface to be related. Recalling that the radius of curvature of a conduit is $C = R$ and for a sphere is $C = R/2$, plots of $1/C$ vs. wt% water can be constructed. Examples for various s/o values with a $a_o = 60\text{Å}^2$ are shown in Fig. 12. Also included are the R_{min} and R_{max} lines for decane as determined experimentally. The single-phase microemulsion forms at the intersection of the minimum radius of curvature R_{min} line with the water radius curve for cylinders. Addition of more water swells the conduits. In terms of the packing constraints alone, conduits remain acceptable structures until R_{max} is reached. In order to accommodate still more water, the microemulsion must rearrange into spheres if R_{max} is not to be

Figure 12. Plots of $1/C$ (C is the radius of curvature) versus weight percent water for various s/o ratios (by weight). $a_o = 60$ Å^2 was used for these curves.

exceeded. Figure 11 also illustrates that, as the oil corner is approached (lower s/o), both the percolation point and the phase boundary occur at lower water content, determined by R_{max}. In reality, the transition from bicontinuous to discrete structures occurs continuously as one moves along water dilution lines toward the water corner.

We also measured the anisotropy of the amphiphilic fluorescence probe p-(trimethylamino)diphenylhexatriene in the DDAB microemulsion [32]. The anisotropy was almost constant when the microemulsions were diluted with oil (constant curvature) but showed a substantial decrease when diluted with water (changing curvature).

The notion of packing constraints associated with impenetrable cylinders and spheres goes a long way toward exploring many of the properties of the DDAB three-component microemulsions. However, many issues remain unresolved. (1) In the illustrations given above, it is assumed that the headgroup area, a_0, is fixed across the entire microemulsion phase. This must be an oversimplification; it is likely that a_0 increases slightly upon addition of water. (2) Counterion specificities and electrostatic interactions in inverted systems remain ill-defined. It is difficult to avoid using empirical R_{min} and R_{max} to define the phase boundaries which must reflect thermodynamic factors which are not explicitly considered in a simple packing model. (3) Only steric (repulsive) interactions between cylinders or spheres are included. (4) Entropic contributions are not considered.

In collaboration with Professor S. Prager, we are presently developing a more sophisticated theory based on a Voronoi tessellation model. We plan to continue this effort and describe this in more detail in the following section.

A major challenge of microemulsion science is understanding the origin of the extraordinarily low interfacial tension encountered in such systems. We measured the interfacial tension [33] between the DDAB microemulsion (AB line) in equilibrium with excess oil and were able to predict how the interfacial tension varied as a function of oil chain length and dilution down the minimum water line. The interfacial tension of these inverted microemulsion structures can be understood in terms of the very large attractive van der Waals forces associated with water-filled conduits cylinders in an oil continuum [34]. Theory shows that for nonconducting cylinders, the Hamaker constant is 40 times larger than for either spheres or bilayers; for conducting conduits the effect is even larger. Under the influence of these extraordinarily large attractive forces, the microemulsion conduits are drawn together, squeezing out excess oil until the oil-swollen surfactant chains from adjacent conduits come into contact. The change in energy associated with this process permits for the first time the quantitative evaluation of interfacial tension in inverted microemulsion phases. While the model contains a number of simplifying assumptions, it does allow delineation of the variation of interfacial tension with oil chain length and the accompanying transistion from conduits to spheres.

The nature of counterion effects in inverted systems is complex. There is no general solution to the Poisson-Boltzmann equation for inverted structures, and even if there were, the extraordinarily high concentration of counterions (4-10 M) encountered in these ionic microemulsions, would make inferences drawn from dilute solution theory suspect. We have characterized DAA microemulsions with chloride and iodide as counterions [35]. Replacement of bromide by chloride results, in some cases, in the formation of multiple single-phase regions and with iodide only a very small one-phase region appears. These systems are also much more susceptible to effects of added electrolytes: above 0.3 M salt, DDAB microemulsions do not form. Thus counterions and salt effects in inverted systems are more pronounced than in amphiphilic structures with normal curvature.

We have also investigated the effect of variations of the chain length of the surfactant [36]. The phase diagram for didecyldimethylammonium, decyldodecyldimethylammonium and hexadecyloctyldimethylammonium bromide were determined. The behavior is complex; in some cases two-phase regions are observed while in others, the microemulsions extend to the water corner rather than to the oil corner. Conductance and NMR diffusion measurements provide information on the changes involved in passing from bicontinuous to water or oil-continuous phases.

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References

[1] Miller, D.D., Bellare, J.R., Evans, D.F., Talmon, Y., Ninham, B.W., J. Phys. Chem. 1987, 91, 647.

[2] Kachar, B., Evans, D.F., Ninham, B.W., J. Colloid Interf. Sci. 1984, 100, 287.

[3] Brady, J., Evans, D.F., Warr, G.G., Greiser, F., Ninham, B.W., J. Phys. Chem. 1986, 90, 1853.

[4] Miller, D.D., "Characterization of Double-Chained Surfactants Using Video Enhanced Microscopy and Time Resolved Fluorescence Quenching," Ph.D. Thesis, University of Minnesota, 1988.

[5] Talmon, Y., Davis, H.T., Scriven, L.E., Thomas, E.L., Rev. Sci. Instrum. 1979, 50, 698.

[6] Talmon, Y., J. Colloid Interf. Sci. 1983, 93, 366.

[7] Evans, D.F., Wightman, P.J., J. Colloid Interf. Sci. 1982, 86, 515.

[8] Beesley, A.H., Ph.D. Thesis, University of Minnesota, 1988.

[9] Evans, D.F., Mitchell, D.J., Ninham, B.W., J. Phys. Chem. 1984, 88, 6344.

[10] Evans, D.F., Langmuir 1988, 4, 3.

[11] Craretto, R., Fernandez-Prini, R., Tapas, M.L., J. Chem. Phys. 1982, 76, 1077.

[12] Ramadan, M., Evans, D.F., Lumry, R., J. Phys. Chem. 1983, 87, 4538.

[13] Evans, D.F., Yamauchi, A., Roman, R., Casassa, E.Z., J. Colloid Interf. Sci. 1982, 86, 89; Evans, D.F., Yamauchi, A., Wei, G.J., Bloomfield, V.A., J. Phys. Chem. 1983, 87, 3537.

[14] Gordon, J.F., The Organic Chemistry of Electrolyte Solution, Wiley, New York, 1975, pp. 158-162.

[15] Mirejovsky, D., Arnett, E.M., J. Am. Chem. Soc. 1983, 105, 112.

[16] Beesley, A.H., Evans, D.F., Laughlin, R.G., J. Phys. Chem. 1988, 92, 791.

[17] Warr, G.G., Evans, D.F., Langmuir 1988, 4, 217.

[18] Miller, D.D., Evans, D.F., J. Phys. Chem., submitted.

[19] Ninham, B.W., Evans, D.F., Wei, G.J., J. Phys. Chem. 1983, 87, 4538.

[20] Hashimoto, S., Thomas, J.K., Evans, D.F., Mukherjee, S., Ninham, B.W., J. Colloid Interf. Sci. 1983, 95, 594.

[21] Evans, D.F., Ninham, B.W., J. Phys. Chem. 1983, 87, 5025.

[22] Talmon, Y., Evans, D.F., Ninham, B.W., Science 1983, 221, 1047.

[23] Miller, D.D., Evans, D.F., Magid, L., manuscript in preparation.

[24] Miller, D.D., Evans, D.F., J. Phys. Chem., submitted.

[25] Evans, D.F., Sen, R., Warr, G.G., J. Phys. Chem. 1986, 90, 5500.

[26] Evans, D.F., Evans, J.B., Sen, R., Warr, G.G., J. Phys. CHem. 1988, 92, 784.

[27] Miller, D.D., Bellare, J.R., Evans, D.F., Talmon, Y., Ninham, B.W., J. Colloid
      Interf. Sci. 1987, 116, 598.

[28] Chen, S.J., Evans, D.F., Ninham, B.W., J. Phys. Chem. 1984, 88, 1631.

[29] Chen, S.J., Evans, D.F., Ninham, B.W., Mitchell, D.J., Blum, F. D., Pickup, S.,
      J. Phys. Chem. 1986, 90, 842.

[30] Evans, D.F., Mitchell, D.J., Ninham, B.W., J. Phys. Chem. 1986, 90, 2817.

[31] Blum, F.D., Pickup, S., Ninham, B.W., Chen, S.J., Evans, D.F., J. Phys. Chem.
      1985, 89, 77.

[32] Chen, V., Warr, G.G., Evans, D.F. and Prendergast, F.G., J. Phys. Chem. 1988, 92,
      768.

[33] Allen, M., Evans, D.F., Mitchell, D.J. and Ninham, B.W., J. Phys. Chem. 1987, 91,
      2320.

[34] Mahanty, J., Ninham, B.W., Dispersion Forces, Academic, New York, 1976.

[35] Brady, J., Evans, D.F., Ninham, B.W., J. Phys. Chem. 1986, 90, 1853.

[36] Warr, G.G., Sen, R., Evans, D.F. and Trend, J.E., J. Phys. Chem. 1988, 92, 774.

ABSTRACTS OF ALL PUBLICATIONS

Direct Visualization Techniques

"Meaning and Structure of Amphiphilic Phases: Inferences from Video-Enhanced Microscopy and Cryo-Transmission Electron Microscopy," D. D. Miller, J. R. Bellare, D. F. Evans, Y. Talmon and B. W. Ninham, J. Phys. Chem. 91, 674 (1987).

This paper attempts to come to grips with a major issue confronting association colloid science. It does so by illustrating some surprising features of aggregates of simple amphiphiles as revealed by two powerful complementary tools, video-enhanced microscopy (VEM) and cryo-transmission electron microscopy (cryo-TEM), both of which allow direct visualization. The natures of these aggregates challenge existing theories, and show up limitations of some other noninvasive, though indirect, techniques. The problem of the meaning of amphiphilic phases and their microstructure is discussed and the necessity for a different descrip-tive language emphasized.

Temperature Dependence and Non-Aqueous Solvents

"Spectroscopic Determination of the Effective Dielectric Constant of Micelle-Water Interfaces between 15 and 85°C," Gregory G. Warr and D. Fennell Evans, Langmuir 4, 217 (1988).

The effective dielectric constant of the interfacial region of several ionic and nonionic micelles has been determined over the range 15-85°C by using two lipophilic, solvatochromic dye probes. Results are measurably different from the results of bulk solvents investigated and are discussed in terms of the model of Mukerjee and Buff for dipoles at interfaces. This model is examined in detail, resulting in improvements to its predictive power. Specific chemical and solubilization location effects in solva-tochromic dye studies of interfacial dielectric constants are also examined in terms of this model. The consequences of the dielectric behavior for headgroup interactions within micelles are discussed.

"Evidence for the Essential Role of Hydrogen Bonding in Promoting Amphiphilic Self-Assembly: Measurements in 3-Methylsydnone," A. H. Beesley, D. F. Evans and R. G. Laughlin, J. Phys. Chem. 92, 791 (1988).

Surface tension and conductance measurements on tetradecylpyridinium nitrate and hexadecylpyridinium bromide and diffusive interfacial transport experiments on dihexa-decyldimethylammonium acetate in 3-methylsydnone are reported. 3-methyl-sydnone is aprotic, possesses a high dielectric constant (144 at 40°C), and has a high cohesive energy density. Unlike hydrogen-bonding solvents of comparable polarity, no evidence for association colloid behavior is detected in 3-methylsydnone. These results confirm previous inferences that hydrogen bonding is a prerequisite for amphiphilic self-assembly.

"Theromodyanmic Properties of the Ethylammonium Nitrate + Water System: Partial Molar Volumes, Heat Capacities, and Expansivities," Martin Allen, D. Fennell Evans and Rufus Lumry, J. Solution Chem. 14, 549 (1985).

Partial molar volumes at 15, 25, and 45°C and partial molar heat capacities and expansivities at 25°C for ethylammonium nitrate + water mixtures are reported. The results are compared with those for other aqueous cosolvents, particularly hydrazine and ammonium nitrate.

Counterion Effects

"Control of Aggregate Structure with Mixed Counterions in an Ionic Double-Chained Surfactant," D. D. Miller, J. R. Bellare, T. Kaneko and D. F. Evans, J. Phys. Chem. (submitted).

The microstructure in dilute aqueous solutions of the ditetradecyldimethylammonium surfactant cation with mixtures of bromide and acetate counterion were studied using video enhanced microscopy, video enhanced microelectrophoresis, cryo-transmission electron microscopy and time resolved fluorescence quenching. A gradual transformation from multilamellar liposomes to first, unilamellar vesicles and microtubules and then, small spherical micelles was seen when the bromide-to-acetate ratio is reduced from unity to zero. Fluorescence quenching reveals that micelles and larger aggregates (i.e. microtubules and vesicles) coexist at intermediate bromide-to-acetate ratios. Electron micrographs of these systems at low bromide-to-acetate ratios are the first ever to reveal the presence of single-component spherical micelles. The results can be explained in terms of increased headgroup and interaggregate repulsions as the bromide ion is replaced by the highly hydrated acetate ion.

"Fluorescence Quenching in Double-Chained Surfactants. I. Theory of Quenching in Micelles and Vesicles," D. D. Miller and D. F. Evans, J. Phys. Chem. (submitted).

The time-resolved fluorescence quenching technique is used to investigate the aggregation behavior of double-chained surfactants. With a new extension of this technique, surfactant solutions consisting of 1) only vesicles, 2) mixtures of vesicles and micelles or 3) only micelles can be distinguished. When applied to solutions of didodecyldimethylammonium acetate, the microstructure is determined to be composed of mainly small micelles over a wide concentration range (0.001 M to 0.1 M); the contribution of vesicles to the total surfactant inventory is quite small. In studies of double-chained surfactants, the technique is particularly valuable for following the transformation of liquid crystalline dispersions to micellar solutions upon heating or dilution.

"Counterion Complexation. Ion Specificity in the Diffuse Double Layer of Surfactant and Classical Colloids," D. Fennell Evans, Joyce B. Evans, Radha Sen and Gregory G. Warr, Physics of Amphiphilic Layers, Proceedings in Physics, Vol. 21, J. Meunier, D. Langevin and N. Boccara, Eds., Springer Verlag, Berlin, 1987, p. 224.

The effect of complexation of alkali metal ions by macrocyclic ligands in dispersions of anionic surfactants and clay colloids has been studied as a route to understanding counterion specific effects in these classes of colloidal dispersions. The rigidity of the lattice of charge in the solid leads to vastly different results than are observed in micellar solutions, where the aggregates rearrange to minimize their free energy.

"Structural Changes in Sodium Dodecyl Sulfate Micelles Induced by Using Counterion Complexation by Macrocyclic Ligands," D. F. Evans, R. Sen and G. G. Warr, J. Phys. Chem. 90, 5500 (1986).

The micellization of SDS in the presence of cryptand C222 and 18-crown-6 was investigated to determine what counterion-specific effects control the aggregation of anionic surfactants. Complexation of the sodium alters the cmc, aggregation number, and ionization of the micelles considerable. The results are discussed in terms of changes in the double layer surrounding the micelle which induce reorganization of the micelle.

"Vesicle and Micelle Formation in a Double-Chained Anionic Surfactant: Counterion Complexation by a Macrocyclic Ligand," D. D. Miller, D. F. Evans, G. G. Warr and J. R. Bellare and B. W. Ninham, J. Colloid & Interf. Sci. 116, 598 (1987).

Addition of the macrocyclic sodium complexing agent cryptand [2.2.2] to aqueous solutions of sodium 8-phenyl-n-hexadecyl-p-sulfonate (Texas No. 1) causes a dramatic decrease in aggregate size, with the formation of unilamellar vesicles and micelles at cryptand to surfactant mole ratios exeeding 0.6. The results can be explained in terms of increased head group repulsion due to removal of the Na^+ counterion from the aggregate surface.

"Counterion Specificity as the Determinant of Surfactant Aggregation, J. E. Brady, D. F. Evans, G. G. Warr, F. Grieser and B. W. Ninham, J. Phys. Chem. 90, 1853 (1986).

Aggregation numbers and critical micelle concentrations are reported for dodecyltrimethylammonium salts with hydroxide and a range of carboxylates as counterion, with and without added salt. The micelles are unusual in that cmcs are higher and the aggregation numbers and ion binding parameters much lower than those for the corresponding bromides. Aggregation numbers change slowly (29 to 49) with added salt up to 1 M. The micellar properties parallel those of corresponding double-chained dimethylammonium salts which exhibit normal behavior (insoluble, lamellar phase) for bromides and anomalous behavior (highly soluble, spontaneous vesciles) for carboxylates and hydroxide. With increasing surfactant concentration the vesicles revert to micelles. An explanation of these phenomena is given.

Microemulsions

"Dynamic Behavior in Hexadecyloctyldimethylammonium Bromide/Alkane/Water Microemulsions," Frank D. Blum, D. Fennell Evans, byaporn Nanagara and Gregory G. Warr, Langmuir, submitted.

Self-diffusion coefficients of oil and water (by pulsed-gradient FT-nmr), and steady-state fluorescence anisotropy results for two solublized probe molecules are reported in microemulsions of hexadecyloctyldimethylammonium bromide ($C_8C_{16}DAB$), alkanes and water. The results show a highly oil-specific effect in microemulsion structure and in the curvature of the surfactant film, leading to the formation of o/w, bicontinuous, and w/o domains depending upon composition and on the nature of the alkane.

"Microemulsion Formation and Phase Behavior of Dialkyldimethylammonium Bromide Surfactants," Gregory G. Warr, Radha Sen, D. Fennell Evans and John E. Trend, J. Phys. Chem. 92, 774 (1988).

The binary and ternary phase behavior of a series of di-n-alkyldimethylammonium bromide surfactants has been investigated. The formation of clear, isotropic microemulsion phases in ternary mixtures with oil and water has been mapped on composition diagrams and this has been correlated with their binary phase behavior in water and with conductivity measurements of the water connectivity in the system.

"Curvature and Geometric Constraints as Determinants of Microemulsion Structure: Evidence from Fluorescence Anisotropy Measurements," Vicki Chen, Gregory G. Warr, D. Fennell Evans and Frank G. Prendergast, J. Phys. Chem. 92, 768 (1988).

Steady-state anisotropy measurements using an amphiphilic fluorescence probe, (trimethylamino)diphenylhexatriene (TMA-DPH) and an oil-soluble probe, diphenylhexatriene (DPH), are reported for three-component microemulsions, employing didodecyldimethylammonium bromide (DDAB) as the surfactant, simple alkanes, and water. The anisotropies of TMA-DPH are almost constant when oil is added to the microemulsions but decrease upon addition of water. The results are interpreted in terms of a structural model based on geometric packing constraints of surfactant-coated cylinders and spheres. The anisotropy shows local changes at the surfactant-water-oil interface which in turn can be related to global structure.

"Interfacial Tension of Ionic Microemulsions," Martin Allen, D. F. Evans, D. J. Mitchell and B. W. Ninham, J. Phys. Chem. 91, 2320 (1987).

Intefacial tension measurements are reported on the system didodecyldimethylammonium bromide/water/alkane against alkane for a range of alkanes and surfactant water ratios. The data span values from low (0.15 dyne/cm) to very low (5×10^{-3} dyne/cm). Physical properties of these microemulsions enable microstructure to be sufficiently well established to correlate interfacial tension with structure. Long range and extremely strong van der Waals forces peculiar to cylindrical geometries have long been known to exist theoretically. These forces operative for high dielectric and/or conducting rods (water) interacting across a low dielectric constant medium (oil) appear necessary to account for the observations.

"Counterion and Co-Ion Specificity in Ionic Microemulsions," V. Chen, D. F. Evans and
B. W. Ninham, J. Phys. Chem. 91, 1823 (1987).

Partial phase diagrams and conductances are reported for three-component microemul-
sions employing didodecyldimethylammonium chloride, bromide, iodide or halide mixtures
as the surfactant. The physical properties and structures of these inverted microemul-
sions exhibit a very large dependence upon counterion and added salt. These effects
illustrate how microemulsion structure can be controlled from the aqueous side of the
oil-water interface.

"Oil, Water, and Surfactant: Properties and Conjectured Structure of Simple Microemul-
sions," D. F. Evans, D. J. Mitchell and B. W. Ninham, J. Phys. Chem. 90, 2817 (1986).

Phase diagrams and physical properties of three-component ionic microemulsions are
reviewed. It is argued that microstructure is set by curvature arising from a balance
between repulsive head group forces and opposing forces due to oil uptake in surfactant
hydrocarbon tails, together with an overriding constraint set by geometric packing. The
picture which emerges is consistent with theories of surfactant-water aggregation and
can be generalized to include multicomponent systems.

"Curvature as a Determinant of Microstructure and Microemulsions," S. J. Chen, D. F.
Evans, B. W. Ninham, D. J. Mitchell, F. D. Blum and S. Pickup, J. Phys. Chem. 90, 842
(1986).

Curvature, set by a balance between repulsive head group forces opposed by hydrocar-
bon chain repulsion augmented by oil uptake in surfactant tails, is shown to be a major
determinant of microemulsion structure. The case is argues through a comparison between
physical properties of three-component systems and those systems in which these proper-
ties are altered by mixed oils, mixed surfactants, cosurfactants, temperature, and oils
which exhibit an extreme affinity for surfactant monolayers. The emerging picture is
consistent with theories of self-assembly for surfactants in water, provided constraints
imposed by geometry are recognized.

Reviews

"A Reappraisal of the Role of Water in Promoting Amphiphilic Assembly and Structure,"
D. F. Evans and D. D. Miller, Water Science Reviews, Vol. 4, F. Franks, Ed., University
Press, Cambridge (submitted).

"Applications of Video and Computer Enhanced Microscopy to Colloid and Interface
Science," D. D. Miller, W. J. Benton, D. F. Evans and S. C. Machuga, AIChE J.
(submitted). Invited review article.

"Self-Organization of Amphiphiles," D. Fennell Evans, Langmuir 4, 3 (1988).

The self-assembly of amphiphiles to form micelles, vesicles, bilayers, and (with added oil) microemulsions is important in biological transformations and in many industrial processes. The hydrocarbon-solvent interactions that drive amphiphilic self-organization in water and other polar hydrogen bonding solvents are discussed. The interactions between aggregates that determine structure and reactivity are described with an emphasis on recent surface forces measurements. Amphiphilic structures determined by video enhanced microscopy (VEM) and cryo-transmission electron microscopy (cryo-TEM) are discussed.

"Vesicles and Molecular Forces," D. F. Evans and B. W. Ninham, Disc. Faraday Society 81, 1 (1986).

Some curious properties of double-chained surfactants which form spontaneous thermodynammically stable unilamellar vesicles in water are reviewed and analyzed in terms of current ideas on self-assembly and recent direct force measurements. The reasons for the apparent success of older theories are discussed. The conclusion, is that the older description in terms of primitive model double layer theory, van der Waals, and additional hydration forces has to be abandoned for a rigorous theory of self-assembly. That conclusion does not abrogate the usefulness of the present theoretical framework in providing a predictive rationale in biological problems. This is illustrated by the use of cationic surfactants as immunosuppressants, bacteriocides, and other applications.

"Molecular Forces in the Self-Organization of Amphiphiles," D. Fennell Evans and B. W. Ninham, J. Phys. Chem. 90, 226 (1986).

Some good progress has been made in quantifying the mechanisms that drive the formation and set the structure of multimolecular aggregates like micelles, vesicles, bilayers, and microemulsions. Parallel advances have been made in understanding the nature of molecular forces between surfaces at distances below 100Å. The interplay between these two areas provides new insights into the way that the physical chemistry of lipid self-assembly affects some biological processes.

LIST OF SCIENTIFIC PERSONNEL

D. Fennell Evans	Professor and PI
Martin Allen	Visiting Professor
David D. Miller	Graduate Student, PhD 1988
Arthur H. Beesley	Graduate Student,
Radha Sen	Postdoctorate
James Rutt	Undergraduate
Gregory G. Warr	Postdoctorate
Ron Benson	Undergraduate
Vicki Chen	Graduate student, PhD, 1988

VITA

D. Fennell Evans

Date of Birth: March 16, 1937

Telephone: (612) 625-6828

Marital Status: Married, one child

Education:

B.A., Pomona College, 1959

Ph.D., Massachusetts Institute of Technology, 1963
Thesis: "Conductance of Ions in Light and Heavy Water"

Employment Experience:

Research Assistant, Massachusetts Institute of Technology
September 1959 - September 1960

N.I.H. Predoctoral Fellow, Massachusetts Institute of Technology
October 1960 - June 1963

Postdoctoral Fellow in Physical Chemistry, Mellon Institute
July 1963 - June 1966

Assistant Professor, Case Western Reserve University
July 1966 - June 1970

Associate Professor, Case Western Reserve University
July 1970 - June 1973

Visiting Professor, University of Bristol, Bristol, England
July 1972 - June 1973

Professor of Chemistry & Chemical Engineering, Carnegie-Mellon University
1973 - 1980

Professor, Department of Chemical Engineering & Materials Science, University
of Minnesota
1980 - present

Professional Activities:

Vice-Chairman (1989) and Chairman (1991) of the Gordon Conference on Micelles and Macromolecular Catalysis.

Member of the Editorial Board, Langmuir, 1987-1990.

Member of the Editorial Board, Water Science Reviews, Cambridge Press, 1984 to present.

Member of the Editorial Board, Journal of Solution Chemistry, 1972 to present.

Director of University of Minnesota Short Course "Colloids and Surface Science," 1981 to present

Willsmore Visiting Professor of Chemistry, University of Melbourne, Melbourne, Australia, Summer 1986.

Visiting Professor, Department of Applied Mathematics, Australian National University, Canberra, Australia, Fall 1984.

Member of Executive Committee, Colloid and Surface Science Section, American Chemical Society, 1979 to 1982.

Chairman of the American Chemical Society LaMer Award Committee (1978).

Founder and Director of the Carnegie-Mellon University Program in Colloids, Polymers and Surfaces, 1973 to 1980, and Short Course "Colloids and Surfaces," 1976 to 1980.

Visiting Professor, University of Bristol, Bristol, England, 1972.

Recipient of an NIH Career Development Award, 1972 to 1977.

NIH Pre-Doctoral Fellowship, 1960 to 1963.

Invited Talks:

Gordon Conference — 1986 — Water Gorden Conference

ACS — 1987 Spring Meeting, Denver — Dennis Symposium on Bioloical Amphiphilic Systems

Les Houche Workshop on Physics of Amphiphilic Layers

Gordon Conference — 1987 — Liposomes and Other Organized Lipid Assemblies

Gordon Conference — 1987 — Micellar and Micromolecular Catalysis

ACS — 1987 Fall Meeting — Langmuir Address

(plus quite a few tallks at ACS, AIChE meetings, seminars and workshop presentations, at companies, U.S. Government meetings and other universities)

Publications:

1. Kay, R. L. and D. F. Evans, "The Association of Tetrabutylammonium Bromide in Methanol-Nitrobenzene Mixtrues," J. Amer. Chem. Soc. 86, 2748 (1964).

2. Evans, D. F., C. Zwaoyski and R. L. Kay, "The Conductance of the Symmetrical Tetraalkylammonium Halides and Picrates in Acetonitrile at 25°," J. Phys. Chem. 69, 3878 (1965).

3. Kay, R. L., C. Zawoyski and D. F. Evans, "The Conductance of the Symmetri cal Tetraalkylammonium Halides and Picrates in Methanol at 25 and 10°," J. Phys. Chem. 69, 4208 (1965).

4. Kay, R. L. and D. F. Evans, "The Conductance of the Tetraalkylammonium Halides in Deuterium Oxide Solutions at 25°." J. Phys. Chem. 69, 4216 (1965).

5. Evans, D. F. and R. L. Kay, "The Conductance Behavior of the Symmetrical Tetraalkylammonium Halides in Aqueous Solution at 25 and 10°," J. Phys. Chem. 70, 366 (1966).

6. Swain, C. G. and D. F. Evans, "Conductance of Ions in Light and Heavy Water at 25°," J. Amer. Chem. Soc. 88, 383 (1966).

7. Kay, R. L. and D. F. Evans, "The Effect of Solvent Structure on the Mobility of Symmetrical Ions in Aqueous Solution," J. Phys. Chem. 70, 2325 (1966).

8. Kay, R. L., T. Vituccio, C. Zawoyski and D. F. Evans, "Viscosity B Coefficients for the Tetraalkylammonium Halides," J. Phys. Chem. 70, 2336 (1966).

9. Evans, D. F., G. P. Cunningham and R. L. Kay, "Interaction of the Tetraethanolammonium Ion with Water as Determined from Transport Properties," J. Phys. Chem. 70, 2974 (1966).

10. Cunningham, G. P., D. F. Evans and R. L. Kay, "Transport Properties of the Tetraethanolammonium Ion in Nonaqueous Solvents at 10 and 25°," J. Phys. Chem. 70, 3998 (1966).

11. Vidulich, G. A., D. F. Evans and R. L. Kay, "The Dielectric Constant of Water and Heavy Water Between 0 and 40°," J. Phys. Chem. 71, 656 (1967).

12. Evans, D. F. and T. L. Broadwater, "The Conductance of Trialkylsulfonium Iodides in Water, Methanol, and Acetonitrile at 10 and 25°," J. Phys. Chem. 72, 1037 (1968).

13. Evans, D. F. and P. Gardam, "Transport Processes in Hydrogen-Bonding Solvents. I. The Conductance of Tetraalkylammonium Salts in Ethanol and Propanol at 25°," J. Phys. Chem. 72, 3281 (1968).

14. Kay, R. L., G. P. Cunningham and D. F. Evans, "The Effect of Solvent Structure on Ionic Mobilities in Aqueous Solvent Mixtures," Hydrogen-Bonded Solvent Systems, 1968, pp. 249-260.

15. Evans, D. F. and P. Gardam, "Transport Processes in Hydrogen-Bonding Solvents. II. The Conductance of Tetraalkylammonium Salts in 1-Butanol and 1-Pentanol at 25°," J. Phys. Chem. 73, 158 (1969).

16. Broadwater, T. L. and D. F. Evans, "Partial Molal Volume of [Bu$_3$N-(CH$_2$)$_8$-NBu$_3$]Br$_2$, a Large Bolaform Electrolyte, in Water at 10 and 25°," J. Phys. Chem. 73, 164 (1969).

17. Kay, R. L., D. F. Evans and G. P. Cunningham, "The Conductance of Large Hydrophobic Ions in Water, Methanol and Acetonitrile at 25°," J. Phys. Chem. 73, 3322 (1969).

18. Broadwater, T. L. and D. F. Evans, "Transport Processes in Hydrogen Bonding Solvents. III. The Conductance of Large Bolaform Ions in Water at 10 and 25°," J. Phys. Chem. 73, 3985 (1969).

19. Thomas, J. and D. F. Evans, "Transport Processe in Hydrogen-Bonding Solvents. IV. Conductance of Electrolytes in Formamide at 25 and 10°," J. Phys. Chem. 74, 3812 (1970).

20. Matesich, M. A., J. A. Nadas and D. F. Evans, "Transport Processes in Hydrogen-Bonding Solvents. V. Conductance of Tetraalkylammonium Salts in 2-Propanol," J. Phys. Chem. 74, 4568 (1970).

21. Cussler, E. L., D. F. Evans and R. G. DePalma, "A Model for Gallbladder Function and Cholesterol Gallstone Formation," Proc. Natl. Acad. of Sci. 67, 400 (1970).

22. Evans, D. F., J. A. Nadas and M. A. Matesich, "Transport Properties in Hydrogen Bonding Solvents. VI. The Conductance of Electrolytes in 2,2,2-Trifluoroethanol," J. Phys. Chem. 75, 1708 (1971).

23. Evans, D. F., J. Thomas, J. A. Nadas and M. A. Matesich, "The Conductance of Electrolytes in Acetone and in 1-Propanol-Acetone Mixtures at 25°," J. Phys. Chem. 75, 1714 (1971).

24. Cussler, E. L., D. F. Evans and M. A. Matesich, "Theoretical and Experimental Basis for a Specific Countertransport System in Membranes," Science 172, 377 (1971).

25. Noveske, T., J. Stuehr and D. F. Evans, "Ion Association and Ultrasonic Relaxation in Hydrogen-Bonding Solvents: 1:1 Electrolytes in 2-Propanol at 25°C," J. Solution Chem. 1, 93 (1972).

26. Evans, D. F., R. G. DePalma, J. A. Nadas and J. Thomas, "The Conductance of Bile Salt-Lecithin-Water Mixtures," J. Solution Chem. 1, 377 (1972).

27. Evans, D. F., S. L. Wellington, J. A. Nadas and E. L. Cussler, "The Conductance of Cyclic Polyether-Cation Complexes," J. Solution Chem. 1, 499 (1972).

28. Evans, D. F. and M. A. Matesich, "The Measurement and Interpretation of Electrolytic Conductance," Techniques of Electrochemistry, Vol. 2, E. Yeager and A. J. Salkind (editors), Wiley Inter-Science, p. 1 (1973).

29. Matesich, M. A., J. Knoefel, H. Feldman and D. F. Evans, "Transport Properties in Hydrogen Bonding Solvents. VII. The Conductance of Electrolytes in 1,1,1,3,3,3-Hexafluoro-2-propanol," J. Phys. Chem. 77, 366 (1973).

30. Stuehr, J., T. Noveske and D. F. Evans, "Ultrasonic Absorption and Rotational Phenomena in Tetraalkylammonium Ions. The Search for Appropriate Models," J. Phys. Chem. 77, 912 (1973).

31. Evans, D. F. and M. A. Matesich, "Ionic Association in Hydrogen-Bonding Solvents," part of Symposium in honor of Henry S. Frank's 70th Birthday, J. Phys. Chem. 2, 193 (1973).

32. Evans, D. F. and E. L. Cussler, "Physiochemical Considerations in Gallstone Pathogenesis," Hospital Practice 9, 133 (1974).

33. Broadwater, T. L. and D. F. Evans, "The Conductance of Divalent Ions in H_2O at 10 and 25°C and in D_2O," J. Solution Chem. 3, 757 (1974).

34. Schiffer, D. K., A. Hochhauser, D. F. Evans and E. L. Cussler, "Concentrating Solutes with Membranes Containing Carriers," Nature 250, 484 (1974).

35. Tao, J. C., E. L. Cussler, and D. F. Evans, "Accelerating Gallstone Dissolution," Proc. Nat. Acad. of Sci. USA 71, 3917 (1974).

36. Choy, E. M., D. F. Evans and E. L. Cussler, "A Selective Membrane for Transporting Sodium Ion Against Its Concentration Gradient," J. Amer. Chem. Soc. 96, 7085 (1974).

37. Cussler, E. L. and D. F. Evans, "How to Design Liquid Membrane Separations," Sep. & Pur. Mtds. 3, 399 (1974).

38. Caracciolo, F., E. L. Cussler and D. F. Evans, "Membranes with Common Ion Pumping," AIChE J. 21, 160 (1975).

39. McElroy, M. I. and D. F. Evans, "The Conductance of Electrolytes in Acetone-2-Propanol and Acetone-1,1,1,3,3,3-Hexafluoro-2-Propanol Mixtures at 25°C," J. Solution Chem. 4, 413 (1975).

40. Schiffer, D. K., E. M. Choy, D. F. Evans and E. L. Cussler, "More Membrane Pumps," AIChE Symposium Series, Water-1974:I. Industrial Waste Treatment 70, 150 (1975).

41. Sehlin, R. C., E. L. Cussler and D. F. Evans, "Diffusion in Bile and Its Implications on Detergency," Biochim. Biophys. Acta 388, 385 (1975).

42. Broadwater, T. L., T. J. Murphy and D. F. Evans, "Conductance of Binary Asymmetric Electrolytes in Methanol," J. Phys. Chem. 80, 753 (1976).

43. Evans, D. F., M. A. Matesich and R. L. Kay, "Ion Solvent Interactions as Determined by Transport Measurements," Solute-Solvent Interactions, J. F. Coetzee and C. D. Riche, editors, 2nd edition, Marcel Dekker Inc., N.Y. (1975).

44. Evans, D. F., M. E. Duffey, K. H. Lee and E. L. Cussler, "Selective Transport of Ions across Liquid Membranes," J. Colloid & Interf. Sci. 5, 119 (1976).

45. Chan, A. F., D. F. Evans and E. L. Cussler, "Explaining Solubilization Kinetics," AIChE J. 22, 1006 (1976).

46. Gilligan, T. J., III., E. L. Cussler and D. F. Evans, "Liquid Membrane Electrodes for Bile Salts," Biochim. Biophys. Acta 497, 627, (1977).

47. Evans, D. F., T. Cha·· and B. C. Lamartine, "The Effect of Charge Upon Mobility: A Critical Examination of the Zwanzig Equation," J. Amer. Chem. Soc. 99, 6492 (1977).

48. Duffey, M. E., D. F. Evans and E. L. Cussler, "Simultaneous Diffusion of Ions and Ion Pairs Across Liquid Membranes," J. Membrane Sci. 3, 1 (1978).

49. Lee, K.-H., D. F. Evans and E. L. Cussler, "Selective Copper Recover with Two Types of Liquid Membranes," AIChE J. 24, 860 (1978).

50. Molnar, W. J., C. P. Wang, D. F. Evans, and E. L. Cussler, "Liquid Membranes for Concentrating Anions Using a Hydroxide Flux," J. Membrane Sci. 4, 129 (1978).

51. Toor, E. W., D. F. Evans, and E. L. Cussler, "Cholesterol Monohydrate Growth in Model Bile Solutions," Proc. Natl. Acad. of Sci. USA, Vol. 75, No. 12, 6230-6234 (December, 1978).

52. Evans, D. F. and T. Tominaga, "Diffusion of Symmetrical and Spherical Solutes in Protic, Aprotic and Hydrocarbon Solvents," J. Solution Chem. 9, 461 (1979).

53. Toor, E. W., D. F. Evans, and E. L. Cussler, "The Nucleation of Cholesterol Monohydrate Crystals in Model Bile Solutions," Hepatology-Research and Clinical Issues, M. M. Fisher (editor) Plenum, New York, Vol. 4, 1979.

54. Evans, D. F., T. Tominaga, J. B. Hubbard, and P. G. Wolynes, "Ionic Mobility – Theory Meets Experiment," J. Phys. Chem. 83, 2669 (1979).

55. Plonski, J. W., J. F. Hoburg, D. F. Evans and E. I. Cussler, "Mixing Liquid Membranes with Electric Fields," J. Membrane Sci. 5, 371 (1979).

56. Tominaga, T., T. B. Stem, Jr. and D. F. Evans, "The Study of Surfactant-Alcohol Mixed Micelles Using conductance, Viscosity, and Electromotive Force Measurements," Bull. Chem. Soc. Jpn. 53, 795-799 (1980).

57. Davis, H. T., T. Tominaga and D. F. Evans, "Correlation Between Tracer Diffusivity, Solvent Viscosity, and Solute Sizes," AIChE J. 26(2), 313-314 (1980).

58. Kale, K. M., E. L. Cussler and D. F. Evans, "Characterization of Micellar Solutions Using Surfactant Ion Electrodes," J. Phys. Chem. 84, 593 (1980).

59. Cussler, E. L. and D. F. Evans, "Liquid Membranes for Separations and Reactions," J. Membrane Sci. 6, 113 (1980)

60. Evans, D. F., T. Tominaga and H. T. Davis, "Tracer Diffusion in Polyatomic Liquids," J. Phys. Chem. 74(2), 1298-1305 (1981).

61. Evans, D. F., S.-H. Chen, G. W. Schriver and E. M. Arnett, "Thermodynamics of Solution of Nonpolar Gases in a Fused Salt. 'Hydrophobic Bonding' Behavior in a Nonaqueous System," J. Amer. Chem. Soc. 103(2), 481 (1981).

62. Weinheimer, R. M., D. F. Evans and E. L. Cussler, "Diffusion in Surfactant Solutions," J. Colloid & Interf. Sci. 80(2), 357-368 (1981).

63. Chen, S.-H., H. T. Davis and D. F. Evans, "Tracer Diffusion in Polyatomic Liquids. II," J. Phys. Chem. 75, 1422 (1981).

64. Huang, C., D. F. Evans and E. L. Cussler, "Linoleic Acid Solubilization with a Spinning Liquid Disc," J. Colloid & Interf. Sci. 82, 499 (1981).

65. Shaeiwitz, J. A., A. F.-C. Chan, E. L. Cussler and D. F. Evans, "The Mechanism of Solubilization in Detergent Solutions," J. Colloid & Interf. Sci. 84, 47 (1981).

66. Evans, D. F., and P. J. Wightman, "Micelle Formation Above 100°C," J. Colloid & Interf. Sci. 86, 515 (1982).

67. Evans, D. F., A. Yamauchi, R. Roman and E. Z. Casassa, "Micelle Formation in Ethylammonium Nitrate, A Low Melting Fused Salt," J. Colloid & Interf. Sci. 86, 89 (1982).

68. Chen, S.-H., D. F. Evans and H. T. Davis, "Tracer Diffusion in Methanol, 1-Butanol and 1-Octanol from 298 to 433 K," AIChE J. 29(4), 640 (1983).

69. Chen, S.-H., H. T. Davis and D. F. Evans, "Tracer Diffusion in Polyatomic Liquids. III," J. Chem. Phys. 77, 2540 (1982).

70. Kale, K. M., E. L. Cussler and D. F. Evans, "Surfactant Ion Electrode Measurements of Sodium Alkylsulfate and Alkyltrimethylammonium Bromide Micellar Solutions," J. Solution Chem. 11, 581 (1982).

71. Mukherjee, S.; D. F. Evans, "Unusual Features of Micellar Diffusion," J. Solution Chem. 12, 871 (1982).

72. Angel, L. R., D. F. Evans, B. W. Ninham, "Three Component Ionic Microemulsions," J. Phys. Chem. 87 538 (1983).

73. Evans, D. F., E. W. Kaler, W. J. Benton, "Liquid Crystals in a Fused Salt: β,γ-Distearoyl Phosphotidylcholine in Ethylammonium Nitrate," <u>J. Phys. Chem.</u> <u>87</u>, 533 (1983).

74. Evans, D. F., S. Mukherjee, D. J. Mitchell and B. W. Ninham, "Surfactant Diffusion: New Results and Interpretations," <u>J. Colloid & Interf. Sci.</u> <u>93</u>, 184 (1983).

75. Evans, D. F., A. Yamauchi, G. J. Wei and V. A. Bloomfield, "Micelle Size in Ethylammonium Nitrate as Determined by Classical and Quasi-Elastic Light Scattering," <u>J. Phys. Chem.</u> <u>87</u>, 3537 (1983).

76. K. Rho, J. M. Lowery, D. F. Evans and E. L. Cussler, "Studies of Model Bile Solutions Using Surfactant Ion Electrodes," <u>J. Phys. Chem.</u> <u>87</u>, 5015 (1983).

77. Talmon, Y., D. F. Evans and B. W. Ninham, "Spontaneous Vesicles from Hydroxide Surfactants: Evidence from Electron Microscopy," <u>Science</u> <u>221</u>, 1047 (1983).

78. Ramadan, M., D. F. Evans and R. Lumry, "Why Micelles Form in Water and Hydrazine: A Reexamination of the Origins of Hydrophobicity," <u>J. Phys. Chem.</u> <u>87</u>, 4538 (1983).

79. Hashimoto, S., J. K. Thomas, D. F. Evans, S. Mukherjee and B. W. Ninham, "Unusual Behavior of Hydroxide Surfactants," <u>J. Colloid & Interface Sci.</u> <u>95</u>, 594 (1983).

80. Ninham, B. W., D. F. Evans and G. J. Wei, "The Curious World of Hydroxide Surfactants: Spontaneous Vesicles or Anomalous Micelles," <u>J. Phys. Chem.</u> <u>87</u>, 5020 (1983).

81. Evans, D. F. and B. W. Ninham, "Ion Binding and The Hydrophobic Effect," <u>J. Phys. Chem.</u> <u>87</u>, 5025 (1983).

82. Chen, S. J., D. F. Evans and B. W. Ninham, "Properties and Structure of Three-Component Ionic Microemulsions," <u>J. Phys. Chem.</u> <u>88</u>, 1621 (1984).

83. Kachar, B., D. F. Evans and B. W. Ninham, "Rapid Characterization of Colloidal Systems by Video Enhanced Light Microscopy," <u>J. Colloid & Intef. Sci.</u> <u>99</u>, 593 (1984).

84. Ramadan, M., D. F. Evans, R. Lumry and S. Philison, "Micelle Formation in Hydrazine-Water Mixtures," <u>J. Phys. Chem.</u> <u>89</u>, 3405 (1985).

85. Wellington, S. L. and D. F. Evans, "The Effect of Pressure and Temperature on Electrolyte Conductance in 2-Propanol," <u>J. Solution Chem.</u> <u>12</u>, 815 (1983).

86. Evans, D. F., M. Allen, B. W. Ninham and A. Fouda, "Critical Micelle Concentrations for the Alkyltrimethylammonium Bromides in Water Over the Temperature Range 25 to 160°C," <u>J. Solution Chem.</u> <u>13</u>, 7 (1984).

87. Kachar, B., D. F. Evans and B. W. Ninham, "Video Enhanced Contrast Differential Interference Microscopy, A New Tool for the Study of Association Colloids and Pre-biotic Assemblies," J. Colloid & Interf. Sci. 100, 287 (1984).

88. Magnuson, D. K., J. W. Bodley and D. F. Evans, "The Activity and Stability of Phosphotase in Alkaline Solution of Water and the Fused Salt, Ethylammonium Nitrate," J. Solution Chem. 13, 583 (1984).

89. Brady, J., D. F. Evans, B. W. Ninham and B. Kachar, "Useful Spontaneous Vesicles," J. Am. Chem. Soc. 106, 4279 (1984).

90. Ninham, B. W., S. J. Chen and D. F. Evans, "Role of Oils and Other Factors in Microemulsion Design," J. Phys. Chem. 88, 5855 (1984).

91. Mitchell, D. J., B. W. Ninham and D. F. Evans, "And Again the Micelle Diffusion Coefficient," J. Colloid & Interf. Sci. 101, 292 (1984).

92. Evans, D. F. and B. W. Ninham, "Ion Binding and Dressed Micelles," J. Phys. Chem. 88, 6344 (1985).

93. Blum, F. D., S. Pickup, B. W. Ninham, S. J. Chen and D. F. Evans, "Structure and Dynamics in Three-Component Microemulsions," J. Phys. Chem. 89, 711 (1985).

94. Evans, D. F., J. Brady, B. Kachar and B. W. Ninham, "Video Enhanced Differential Interference Contrast Microscopy: Characterizing Colloidal Materials," J. Solution Chem. 14, 142 (1985).

95. Allen, M., D. F. Evans and R. Lumry, "Thermodynamic Properties of Ethylammonium Nitrate + Water System: Partial Molar Volumes, Heat Capacities, and Expansivities," J. Solution Chem. 14, 549 (1985).

96. Pashley, R. M., P. M. McGuiggan, B. W. Ninham and D. F. Evans, "Attractive Forces Between Uncharged Hydrophobic Surfaces: Direct Measurements in Aqueous Solution," Science 221, 1047 (1983).

97. Drummond, C. J., G. G. Warr, F. Grieser, B. W. Ninham and D. F. Evans, "The Surface Properties and Micellar Interfacial Microenvironment of N-Dodecyl β-D-Maltoside," J. Phys. Chem. 89, 2103 (1985).

98. Evans, D. F. and B. W. Ninham, "Molecular Forces in the Self-Organization of Amphiphiles," J. Phys. Chem. 90, 226 (1986).

99. Brady, J., D. F. Evans, G. Warr, F. Greiser and B. W. Ninham, "Counterion Specificity as the Determinant of Surfactant Aggregation," J. Phys. Chem. 90, 1853 (1986).

100. Chen, S. J., D. F. Evans, B. W. Ninham, D. J. Mitchell, F. D. Blum and S. Pickup, "Curvature as a Determinant of Microstructure and Microemulsions," J. Phys. Chem. 90, 842 (1986).

101. Evans, D. F., D. J. Mitchell and B. W. Ninham, "Oil, Water and Surfactant: Properties and Conjectured Structure of Simple Microemulsions," J. Phys. Chem. 90, 2817 (1986).

102. Pashley, R. M., P. M. McGuiggan, B. W. Ninham, J. Brady and D. F. Evans, "Direct Measurements of Surface Forces Between Bilayers of Double-Chained Quaternary Ammonium Acetate and Bromide Surfactants," J. Phys. Chem. 90, 1637 (1986).

103. Warr, G. G., C. J. Drummond, F. Grieser, B. W. Ninham and D. F. Evans, "Aqueous Solution Properties of Nonionic n-Dodecyl β-D-Maltoside Micelles, J. Phys. Chem. 90, 4581 (1986).

104. Warr, G. G., F. Grieser and D. F. Evans, "Determination of Micelle Size and Polydispersity by Fluorescence Quenching: Experimental Results," J. Chem. Soc. Trans. Faraday I 82, 1829 (1986).

105. Evans, D. F. and B. W. Ninham, "Vesicles and Molecular Forces," Disc. Faraday Society 81, 1 (1986).

106. Miller, D. D., D. F. Evans, G. G. Warr, J. R. Bellare and B. W. Ninham, "Vesicle and Micelle Formation in a Double-Chained Anionic Surfactant: Counterion Complexation by a Macrocyclic Ligand," J. Colloid & Interf. Sci. 116, 598 (1987).

107. Evans, D. F., R. Sen and G. G. Warr, "Structural Changes in SDS Micelles Induced Using Counterion Complexation by Macrocyclic Ligands," J. Phys. Chem. 90, 5500 (1986).

108. Miller, D. D., J. R. Bellare, D. F. Evans, Y. Talmon and B. W. Ninham, "On the Meaning and Structure of Amphiphilic Phases: Inferences from Video Enhanced Microscopy and Cryo-Transmission Electron Microscopy," J. Phys. Chem. 91, 674 (1987).

109. Chen, V., D. F. Evans and B. W. Ninham, "Counterion and Co-Ion Specificity in Ionic Microemulsions," J. Phys. Chem. 91, 1823 (1987).

110. Allen, M., D. F. Evans, D. J. Mitchell and B. W. Ninham, "Interfacial Tension of Ionic Microemulsions," J. Phys. Chem. 91, 2320 (1987).

111. Evans, J. B. and D. F. Evans, "A Comparison of Surfactant Counterion Effects in Water and Formamide," J. Phys. Chem. 91, 3820 (1987).

112. Warr, G. G. and D. F. Evans, "Spectroscopic Determination of the Effective Dielectric Constant of Micelle-Water Interfaces Between 15 and 85°C," Langmuir 4, 217 (1988).

113. Evans, D. F., "Self-Organization of Amphiphiles," Langmuir Lecture, Langmuir 4, 3 (1988).

114. Chen, V., G. G. Warr, D. F. Evans and F. G. Prendergast, "Three-Component Microemulsion Structure: Curvature and Geometric Constraints," Physics of Amphiphilic Layers, Proceedings in Physics, Vol. 21, J. Meunier, D. Langevin and N. Boccara, Eds., Springer Verlag, Berlin, 1987, p. 328.

115. Miller, D. D., J. R. Bellare, D. F. Evans, Y. Talmon and B. W. Ninham, "Direct Visualization of Amphiphilic Phases by Video Enhanced Microscopy and Cryo-Transmission Electron Microscopy," Physics of Amphiphilic Layers, Proceedings in Physics, Vol. 21, J. Meunier, D. Langevin and N. Boccara, Eds., Springer Verlag, Berlin, 1987, p. 202.

116. Evans, D. F., J. B. Evans, R. Sen and G. G. Warr, "Counterion Complexation Ion Specificity in the Diffuse Double Layer of Surfactant and Classical Colloids," Physics of Amphiphilic Layers, Proceedings in Physics, Vol. 21, J. Meunier, D. Langevin and N. Boccara, Eds., Springer Verlag, Berlin, 1987, p. 224.

117. Chen, V., D. F. Evans, G. G. Warr and F. G. Prendergast, "Curvature and Geometric Constraints as Determinants of Microemulsion Structure: Evidence from Fluorescence Anisotropy Measurements," J. Phys. Chem. 92, 768 (1988).

118. Evans, D. F., J. B. Evans, R. Sen and G. G. Warr, "A Comparison of Counterion Effects in Surfactant and Classical Colloid Systems," J. Phys. Chem. 92, 784 (1988).

119. Warr, G. G., R. Sen, D. F. Evans and J. E. Trend, "Microemulsion Formation and Phase Behavior of Dialkyldimethylammonium Bromide Surfactants," J. Phys. Chem. 92, 774 (1988).

120. Beesley, A. H., D. F. Evans and R. G. Laughlin, "Evidence for the Essential Role of Hydrogen Bonding in Promoting Amphiphilic Self-Assembly: Measurements in 3-Methylsydnone," J. Phys. Chem. 92, 791 (1988).

121. Payne, K. A., L. J. Magid and D. F. Evans, "Structural Changes in Anionic Micelles Induced by Counterion Complexation with a Macrocyclic Ligand: A Neutron Scattering Study," Progr. in Colloid & Polymer Sci. 73, 10 (1987).

122. Blum, F. D., D. F. Evans, B. Nanagara and G. G. Warr, "Dynamic Behavior in Hexadecyloctyldimethylammonium Bromide/Alkane/Water Microemulsions," Langmuir, submitted.

123. Miller, D. D. and D. F. Evans, "Fluorescence Quenching in Double-Chained Surfactants. I. Theory of Quenching in Micelles and Vesicles," J. Phys. Chem., submitted.

124. Evans, D. F. and D. D. Miller, "A Reappraisal of the Role of Water in Promoting Amphiphilic Assembly and Structure," Water Science Reviews, Volume 4, F. Franks, Ed., University Press, Cambridge, submitted.

125. Miller, D. D., D. F. Evans and L. J. Magid, "Fluorescence Quenching in Double-Chained Surfactants. II," J. Phys. Chem., submitted.

126. Miller, D. D., W. J. Benton, D. F. Evans and S. C. Machuga, "Applications of Video and Computer Enhanced Microscopy to Colloid and Interface Science," AIChE J., submitted.

127. Miller, D. D., J. R. Bellare, T. Kaneko and D. F. Evans, "Control of Aggregate Structure with Mixed Counterions in an Ionic Double-Chained Surfactant," J. Phys. Chem., submitted.